

PATENT ABSTRACTS OF JAPAN

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(54) LUMINOUS PHOSPHOR

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a luminous phosphor activated with bivalent europium, having a specific chemical compositional formula, thus attaining long afterglow time/high afterglow luminance compared to conventional silicate-based luminous phosphors, presenting diversified luminescent colors ranging from blue to yellowish green colors, therefore useful for e.g. night signs.

SOLUTION: This luminous phosphor is such one as to be activated with bivalent europium and have a chemical composition of the formula $(R)_a(O)_{1-a}(Mg_{1-x}Zn_x)_b(O)_{1-b}Si_c(Ge)_dEu_{1-x-y}M$ (R is at least one element selected from the group consisting of Ca, Sr and Ba; M is a coactivator, being at least one element selected from the group consisting of Nb, Zr, Bi, Mn, Sn, In, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y; $0.4 \leq (a) \leq 0.9$; $0.00001 \leq b \leq 0.30$; $0.25 \leq c \leq 1.5$; $0.00001 \leq d \leq 0.2$; $0.00001 \leq e \leq 0.2$; $0 \leq x < 1.0$; $0 \leq y < 1.0$). This luminous phosphor is obtained by the following process: appropriate amounts of respective specified stocks are weighed, mixed together, put into an alumina crucible, and then burned at 950–1,500° C for 1–12 h in a reductive atmosphere.

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CLAIMS

[Claim(s)]

[Claim 1] Activation is carried out with divalent europium. A chemical composition type $a\text{RO}$, $O-b\text{Al}_2\text{O}_3$, $c(\text{Si}_{1-y}\text{Ge}_y)\text{O}_2$, and $d\text{Eu}-e\text{M}$ (However, R is at least one sort chosen from the group which consists of Ba, Sr, and calcium, and M is a coactivator.) It is shown. at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, In, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y -- it is -- a, b, c, d, ex, and y are phosphorescent materials characterized by being in the range of $0.4 \leq a \leq 0.9$, $0.00001 \leq b \leq 0.30$, $0.25 \leq c \leq 1.5$, $0.00001 \leq d \leq 0.2$, $0.00001 \leq e \leq 0.2$, $0 \leq x < 1.0$, and $0 \leq y < 1.0$, respectively.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Activation of this invention is carried out with divalent europium. A chemical composition type aRO, O-bAl₂O₃, c(Si₁-yGe_y) O₂, and dEu-eM (However, R is at least one sort chosen from the group which consists of Ba, Sr, and calcium, and M is a coactivator.) It is shown, at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, In, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y — it is — by long afterglow time amount and quantity afterglow brightness It is related with phosphorescent materials with various luminescence wavelength.

[0002]

[Description of the Prior Art] the phenomenon in which, as for fluorescence, the matter emits the light near a visible region by the stimulus (excitation) from the outside — it is — a fluorescent lamp, a discharge lamp, and CRT (Cathode Ray Tube) — the so-called luminescence of the Braun tube etc. is this. Although the matter which emits fluorescence is called fluorescent substance, this is called phosphorescence when the fluorescence of the time amount (about 0.1 seconds) of extent sensed for an eye after an excitation halt continues. Moreover, the phosphorescent substance with high-persistence from which the time amount which phosphorescence follows, i.e., afterglow time amount, reaches in several hours at a room temperature is called phosphorescent materials.

[0003] It is put in practical use as phosphorescent materials and the sulfide system phosphorescent materials represented by ZnS:Cu serve as the current mainstream. Although ZnS:Cu sulfide phosphorescent materials are put in practical use dozens of years before, afterglow time amount has the trouble of being short in about at most 3 hours. Moreover, the decomposition reaction which becomes ZnS+H₂O → Zn+H₂S arises with the ultraviolet rays included in daylight, and the moisture contained in atmospheric air, the luminous object itself carries out melanism of these phosphorescent materials, and they have the fatal fault that an afterglow function falls remarkably for a short period of time. Furthermore, in order to compensate short afterglow time amount, the radioactive substance may be made to contain and there was also demerit of being harmful, to the body or an environment. Therefore, this kind of phosphorescent materials were mainly used only for applications restricted very much, such as the watch with a luminous dial and indoor Nighttime display.

[0004] Recently, the new phosphorescent materials (JP.9-194833A, JP.9-241631A) which make silicate the subject were developed. As compared with the conventional sulfide system, by high afterglow brightness, these phosphorescent materials have long afterglow time amount, and since they are oxides, they have the property with them of excelling also in chemical durability. For this reason, in addition to applications, such as the existing watch with a luminous dial and the indoor Nighttime display, broad applications, such as a display, accessories, etc. of a disaster prevention indicator and the safety for location recognition, are expectable.

[0005]

[Problem(s) to be Solved by the Invention] Thus, a property needs to be improved according to a request as the applicable field of phosphorescent materials is expanded. The further

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[0012] x can realize long afterglow time amount and quantity afterglow brightness also by showing the substitutional rate when permuting Mg by Zn, and permuting some Mg by Zn. In addition, although the permutation by Zn is a partial permutation of an indispensable component, if Mg tends to acquire said better property, the range of 0<x<0.5 will be desirable especially desirable, and the range of it will be 0<x<0.2.

[0013] y can realize long afterglow time amount and quantity afterglow brightness also by showing a substitutional rate in case germanium permutes Si, and permuting a part of Si by germanium. In addition, although the permutation by germanium is a partial permutation of an indispensable component, if Si tends to acquire said better property, the range of 0<y<0.5 will be desirable especially desirable, and the range of it will be 0<y<0.2.

[0014] Moreover, in case the phosphorescent materials of this invention are compounded, phosphate, such as boric acid and ammonium dihydrogenphosphate, etc. can be added as flux. The optimal addition is 0.05 ~ 8% of range in mol%.

[0015]

[Embodiment of the Invention] An oxide, a carbonate, a nitrate, a hydroxide, etc. can be used for the raw material of the phosphorescent materials of this invention. After carrying out specified quantity weighing capacity of these raw materials and fully mixing with a ball mill etc., it puts into an alumina crucible and calcinates at 950~1500 degrees C among the reducing atmosphere of hydrogen gas etc. for 1 to 12 hours. The baking object obtained depending on the case can also be ground and re-calcinated, and this can also be repeated twice or more. In that case, an oxidizing atmosphere is sufficient as intermediate baking, and it should just be reducing atmosphere in the last baking.

[0016] As for the synthetic approach of ceramic fine particles, the sol gel process, the wet synthesis method (coprecipitation method), etc. are known. The phosphorescent materials of this invention can also be compounded by these approaches, if it is presentation within the limits indicated by the claim of this invention, it can make with the synthesis method of general ceramic fine particles, and it is not limited to the solid reaction method mentioned above. Hereafter, although a concrete example explains this invention, this invention is not limited only to these examples.

[0017]

[Example]

[Example 1]

SrCO₃ 0.194gMgO(s) 0.761gAl₂O₃ 0.214gSiO₂(s) 2.395gH₃BO₃ 0.259gEu(s) 0.203 0.015gTm(s) 203 Mix enough the raw material of a combination presentation of 0.182g above, put into an alumina crucible, and it calcinates at 1350 degrees C in the mixed-gas air current of H₂ 2+3% of N 97% for 3 hours. The phosphorescent materials used as chemical composition type 0.690SrO, 0.310MgO, 0.0345aluminum2O3, 0.656SiO₂, 0.0345 B-2O₃, 0.00138Eu, and 0.0138Tm were obtained.

[0018] These phosphorescent materials are excited with the light of a fluorescent lamp, and the emission spectrum 1 minute after an exposure halt is shown in drawing 1. Measurement was performed using the spectrophotofluorometer. An emission peak wavelength is near 480nm, and blue luminescence was observed visually. Moreover, the excitation spectrum measured in the luminescence wavelength of 480nm is shown in drawing 2. This spectrum shows excitation wavelength having spread to the visible region and being easily excited with light, such as sunlight and a fluorescent lamp.

[0019] The phosphorescent materials of an example 1 and the example A of a comparison are excited for 20 minutes by 200lx(es) using a fluorescent lamp, and aging of the afterglow brightness from immediately after an excitation halt is shown in drawing 3. Measurement was performed using the luminance meter (LS-100 and Minolta Co., Ltd.). A ***** understands [drawing / this] afterglow time amount for the phosphorescent materials of an example 1 by high brightness from the example A of a comparison. In addition, the examples A of a comparison are the phosphorescent materials of an OKERU dynamite presentation.

[0020] An example 1, the examples 2-5 which show the same luminescent color, and the example A of a comparison were produced by the same approach as an example 1. These

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improvement in afterglow brightness and afterglow time amount is strongly desired also in it. [0006]

[Means for Solving the Problem] In order that this invention may solve the above-mentioned technical problem, activation is carried out with divalent europium. The chemical composition type is aRO, O-bAl₂O₃, c(Si₁-yGe_y) O₂, and dEu-eM (however, R is at least one sort chosen from the group which consists of Ba, Sr, and calcium, and M is a coactivator), at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, In, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y — it is — it is going to offer the phosphorescent materials shown. [0007] The crystal phase which serves as a subject of said silicate phosphorescent materials (JP.9-194833A) is the mineral called akermanite (calcium2Mg (Si 2O₇)), the congruence pyramid of Si 2O₇ and MgO₄ tetrahedron built the layer (Si2MgO₇) with O share, and, as for this crystal structure, calcium is contained by 8 coordination between layers. Sr and Ba can be dissolved in calcium location between this layer, and it becomes akermanite and the structure of isomorphism.

On the other hand, generally the mineral called a GERE night (calcium2aluminum (AlSiO₇)) is known. The congruence pyramid of 2 (aluminum, SiO₇) and AlO₄ tetrahedron built the layer (SiAl 2O₇) with O share, and, as for this crystal structure, calcium is contained by 8 coordination between layers. Sr and Ba can be dissolved also in calcium location between this layer, and it becomes a GERE night and the structure of isomorphism. The crystal structure to which aluminum dissolved continuously is called melilite by making these two crystal phases into an member. That is, the congruence pyramid of 2 (aluminum, SiO₇) and O(Mg, aluminum)4 tetrahedron build a layer (3 (Si, aluminum, MgO₇) with O share, and calcium, Sr, and Ba enter by 8 coordination between layers. We came to complete a header and this invention for the phosphorescent materials which can solve a technical problem by considering this melilite mold structure as a mother crystal, and using divalent europium as an activator.

[0008] Namely, phosphorescent materials according to claim 1 Activation is carried out with divalent europium. The chemical composition type aRO, O-bAl₂O₃, c(Si₁-yGe_y) O₂, and dEu-eM (However, R is at least one sort chosen from the group which consists of Ba, Sr, and calcium, and M is a coactivator.) It is shown, at least one sort chosen from the group which consists of Nb, Zr, Bi, Mn, Sn, In, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y — it is — That a, b, c, d, ex, and y are in the range of 0.4<a<0.9, 0.00001<b<0.30, 0.25<c<1.5, 0.00001<d<0.2, 0.00001<e<0.2, 0<x<1.0, and 0<y<1.0, respectively They are the phosphorescent materials by which it is characterized.

[0009] In the phosphorescent materials of this invention, in a, b shows the presentation ratio of aluminum 2O₃, and, as for (1-a), c shows [the presentation ratio of RO (however, R is at least one sort chosen from the group which consists of Ba, Sr, and calcium)] the presentation ratio of SiO₂ and/or GeO₂ for the presentation ratio of MgO and/or ZnO. The range of a, b, and c serves as melilite mold structure in 0.4<a<0.9, 0.00001<b<0.30, and 0.25<c<1.5, and the phosphorescent materials of high afterglow brightness and long afterglow time amount can be obtained. It becomes the phosphorescent materials which have the broad luminescent color of blue ~ yellowish green by changing the ratio of Ba, Sr, and calcium in R. By the Sr independent, it is blue luminescence, and luminescence wavelength is shifted to a long wavelength side in permuting Sr gradually from calcium, and, specifically, luminescence wavelength is shifted to a short wavelength side by permuting Sr gradually by Ba. Moreover, also by changing the presentation ratio of aluminum 2O₃, luminescence wavelength can be shifted and the phosphorescent materials which have the desired luminescent color can be obtained.

[0010] d must show the concentration of an activator and the range of it must be 0.00001<d<0.2. Light absorption worsens in d<0.00001, and sufficient afterglow brightness is not obtained, but a lifting and afterglow brightness fall concentration quenching by d>0.2 conversely, desirable — 0.00005<d<0.1 — it is the range of 0.0001<d<0.05 especially preferably.

[0011] e must show the concentration of a coactivator and the range of it must be 0.00001<e<0.2. The effectiveness of increasing afterglow time amount and afterglow brightness in e<0.00001 is scarce, and afterglow brightness falls gradually by e>0.2 conversely, desirable — 0.0001<e<0.15 — it is the range of 0.002<e<0.10 especially preferably.

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presentations are shown in Table 1. The empirical formula shows two kinds about each example, and is written in the form where the upper case corresponded with the chemical composition type, and the lower berth corresponded with the crystal structure. It excited for 20 minutes by 200lx(es) using the fluorescent lamp to each phosphorescent materials, and the afterglow brightness from immediately after an excitation halt was measured with the luminance meter. The relative afterglow brightness shown in Table 1 is the relative value which expressed the afterglow brightness of the example A of a comparison as 100 in the afterglow brightness 10 minutes after an excitation halt.

[0021]

[Table 1]

実例	組成式	相対発光輝度(%)
1	0.690SrO・0.310MgO・0.0345Al ₂ O ₃ ・0.656SiO ₂ ・0.0345B ₂ O ₃ ・0.00138Eu・0.0138Tm Sr _{0.690} Al _{0.310} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	350
2	0.693SrO・0.331MgO・0.00335Al ₂ O ₃ ・0.668SiO ₂ ・0.00335B ₂ O ₃ ・0.00134Eu・0.0134Tm Sr _{0.693} Al _{0.331} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	200
3	0.714SrO・0.286MgO・0.0714Al ₂ O ₃ ・0.643SiO ₂ ・0.0357B ₂ O ₃ ・0.00143Eu・0.0143Tm Sr _{0.714} Al _{0.286} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	375
4	0.741SrO・0.259MgO・0.111Al ₂ O ₃ ・0.630SiO ₂ ・0.0371B ₂ O ₃ ・0.00148Eu・0.0148Tm Sr _{0.741} Al _{0.259} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	275
5	0.769SrO・0.231MgO・0.154Al ₂ O ₃ ・0.615SiO ₂ ・0.0385B ₂ O ₃ ・0.00154Eu・0.0154Tm Sr _{0.769} Al _{0.231} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	200
比較例 A	0.667SrO・0.333MgO・0.667SiO ₂ ・0.0333B ₂ O ₃ ・0.00133Eu・0.0133Tm Sr _{0.667} Al _{0.333} Si _{0.182} O ₇ ・0.1B ₂ O ₃ ・0.004Eu・0.040Tm	100

[0022] About an example 5 and the example A of a comparison, X diffraction measurement is performed and the obtained spectrum is shown in drawing 4. From this drawing, whenever [angle-of-diffraction / of an example 5] differs from the example A of a comparison clearly, and, as for the example A of a comparison, it turns out that it has become another structure, i.e., melilite mold structure.

[0023] In each example and the example A of a comparison which were shown in Table 1, it becomes common as Sr₂Mg₁-nAl₂Si₂-mO₇, 0.1 B-2O₃, 0.004Eu, and 0.040Tm, the empirical formula expressed with the crystal structure is shown, and what plotted relative afterglow brightness to this n is shown in drawing 5. This n expresses the substitutional rate of the GERE night presentation over an akermanite presentation. The afterglow brightness of a melilite presentation (0<n<1) is high, and is afterglow brightness high twice in addition from the afterglow brightness of an akermanite (n=0) presentation also in the 3.75 times greatest by n=0.2, and n=0.4 so that clearly from this drawing.

[0024]

[Example 6]

SrCO₃ 4.889gCaCO₃(s) 3.105gMgO(s) 0.801gAl₂O₃ 0.225gSiO₂(s) 2.521gH₃BO₃ 0.273gEu(s) 203 0.016gTm(s) 203 Mix enough the raw material of a combination presentation of 0.170g above, put into an alumina crucible, and it calcinates at 1300 degrees C in the mixed-gas air current of H₂ 2+3% of N 97% for 3 hours. The phosphorescent materials used as chemical composition type 0.518SrO, 0.173CaO, 0.310MgO, 0.0345aluminum2O3, 0.656SiO₂, 0.0345 B-2O₃, 0.00138Eu, and 0.0138Tm were obtained.

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[0025] These phosphorescent materials are excited with the light of a fluorescent lamp, and the emission spectrum 1 minute after an excitation halt is shown in drawing 8. Measurement was performed using the spectrophotofluorometer. An emission peak wavelength is near 490nm, and luminescence of a bluish green color was observed visually.

[0026] Examples 7-14 were produced by the same approach as an example 6. These presentations are shown in Table 2. It excited for 20 minutes by 200lx(es) using the fluorescent lamp to each phosphorescent materials, and the afterglow brightness from immediately after an excitation halt was measured with the luminance meter. The relative afterglow brightness shown in the table is the relative value which expressed the afterglow brightness of the example B of a comparison as 100 in the afterglow brightness 10 minutes after an excitation halt.

[0027]

[Table 2]

実施例	組成式	相対残光 輝度(%)
6	$0.690(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.310\text{MgO} \cdot 0.0345\text{Al}_2\text{O}_3 \cdot 0.656\text{SiO}_2 \cdot 0.0345\text{B}_2\text{O}_3 \cdot 0.00138\text{Eu} \cdot 0.0138\text{Tm}$	6 0 0
7	$0.714(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.286\text{MgO} \cdot 0.0714\text{Al}_2\text{O}_3 \cdot 0.643\text{SiO}_2 \cdot 0.0357\text{B}_2\text{O}_3 \cdot 0.00143\text{Eu} \cdot 0.0143\text{Tm}$	5 6 0
8	$0.769(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.231\text{MgO} \cdot 0.154\text{Al}_2\text{O}_3 \cdot 0.615\text{SiO}_2 \cdot 0.0385\text{B}_2\text{O}_3 \cdot 0.00154\text{Eu} \cdot 0.0154\text{Tm}$	3 6 0
9	$0.667(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.333\text{MgO} \cdot 0.667\text{SiO}_2 \cdot 0.0333\text{B}_2\text{O}_3 \cdot 0.00133\text{Eu} \cdot 0.0133\text{Tm}$	1 2 0
10	$0.714(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.286\text{MgO} \cdot 0.0714\text{Al}_2\text{O}_3 \cdot 0.643\text{SiO}_2 \cdot 0.0357\text{B}_2\text{O}_3 \cdot 0.00143\text{Eu} \cdot 0.0143\text{Tm}$	8 0 0
11	$0.667(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.333\text{MgO} \cdot 0.667\text{SiO}_2 \cdot 0.0333\text{B}_2\text{O}_3 \cdot 0.00133\text{Eu} \cdot 0.0133\text{Tm}$	1 4 0
12	$0.714(\text{Sr}_{0.7}\text{Ba}_{0.3})\text{O} \cdot 0.286\text{MgO} \cdot 0.0714\text{Al}_2\text{O}_3 \cdot 0.643\text{SiO}_2 \cdot 0.0357\text{B}_2\text{O}_3 \cdot 0.00143\text{Eu} \cdot 0.0143\text{Tm}$	9 0 0
13	$0.714\text{SrO} \cdot 0.286(\text{Mg}_{0.7}\text{Ba}_{0.3})\text{O} \cdot 0.0714\text{Al}_2\text{O}_3 \cdot 0.643\text{SiO}_2 \cdot 0.0357\text{B}_2\text{O}_3 \cdot 0.00143\text{Eu} \cdot 0.0143\text{Tm}$	2 0 0
14	$0.714(\text{Sr}_{0.7}\text{Ba}_{0.3})\text{O} \cdot 0.286\text{MgO} \cdot 0.0714\text{Al}_2\text{O}_3 \cdot 0.643\text{SiO}_2 \cdot 0.0357\text{B}_2\text{O}_3 \cdot 0.00143\text{Eu} \cdot 0.0143\text{Tm}$	2 2 0
比較例 B	$0.667(\text{Sr}_{0.7}\text{Ca}_{0.3})\text{O} \cdot 0.333\text{MgO} \cdot 0.667\text{SiO}_2 \cdot 0.0333\text{B}_2\text{O}_3 \cdot 0.00133\text{Eu} \cdot 0.0133\text{Tm}$	1 0 0

[0028] The emission spectrum measured about the phosphorescent materials of examples 10, 12, and 14 is shown in drawing 7, and 8 and 9, respectively. Measurement was excited by the fluorescent lamp and performed the emission spectrum 1 minute after an excitation halt with the spectrophotofluorometer. In drawing 7, an emission peak wavelength is in 505nm, and green luminescence was observed visually. In drawing 8, an emission peak wavelength is in 520nm, and yellowish green luminescence was observed visually. In drawing 9, an emission peak wavelength is in 488nm, and dark blue luminescence was observed visually. Thus, various luminescence from blue to yellowish green is realizable by permuting Sr by calcium and Ba.

[0029]

[Effect of the Invention] This invention is constituted as mentioned above, and it has the effectiveness indicated below. Since the phosphorescent materials by this invention realize long afterglow time amount and quantity afterglow brightness compared with the conventional silicate phosphorescent materials and have the various luminescent color from blue to yellowish green, a broad application can be provided with them.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is an emission spectrum 1 minute after [of an example 1] an optical-pumping halt.

[Drawing 2] It is an excitation spectrum in the luminescence wavelength of 480nm of an example 1.

[Drawing 3] It is the graph which showed aging of the afterglow brightness of an example 1 and the example A of a comparison.

[Drawing 4] It is the X diffraction Fig. of an example 5 and the example A of a comparison.

[Drawing 5] It is the graph which plotted the relative afterglow brightness 10 minutes after an excitation halt to n in $\text{Sr}_2\text{Mg}_1\text{-nAl}_2\text{ZnSi}_2\text{-nO}_7$, 0.1 B-2O₃, 0.004Eu, and 0.040Tm.

[Drawing 6] It is an emission spectrum 1 minute after [of an example 6] an optical-pumping halt.

[Drawing 7] It is an emission spectrum 1 minute after [of an example 10] an optical-pumping halt.

[Drawing 8] It is an emission spectrum 1 minute after [of an example 12] an optical-pumping halt.

[Drawing 9] It is an emission spectrum 1 minute after [of an example 14] an optical-pumping halt.

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